



Short communication

Proton transfer in the interface of Nafion and sulfonated polypyrrolone

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HIGHLIGHTS

- Proton resistance increased due to phase separation at different polymer interface.
- Phase separation is adverse to proton transfer process between different polymers.
- Continuous distribution of polymer is needed for good proton conduction.

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ABSTRACT

The proton conductivity at the interface of Nafion and sulfonated polypyrrolone composite membrane decreases by 56% from 0.039 S cm^{-1} to 0.017 S cm^{-1} , due to phase separation after annealing this binary composite membrane at 140°C , which is 10°C above the glass transition temperature of Nafion polymer. After annealing the membrane, the change in the relative intensity of the lower angles of the X-ray diffraction (XRD) peaks located at ca. 11.9° , 17.5° and 19.7° indicates an increase of the low spacing region for the polymer chains of the composite membrane and atomic force microscopy (AFM) measurement depicts a morphological evolution from an uniform dispersion to a spherules micro-structure, implying the aggregation of polymer chains of the annealed composite membrane. These results are combined to reveal there is a microphase separation of this binary composite membrane as it is annealed at 140°C .

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1. Introduction

In the request for alternative means to generate energy, direct methanol fuel cell (DMFC) is one of the most promising candidates. Recently, a lot of proton conductive polymers, e.g., the sulfonated polypyrrolone (sPPL) [1,2], sulfonated poly (ether ether ketone) (SPEEK) [3], sulfonated polyimide (sPI) [4] etc., are developed, exhibiting low methanol permeation (LMP) and better performances with respect to Nafion. However, it is still difficult to apply these LMP membranes in DMFC. On the one hand, there is always a compromise between the satisfied low methanol permeability obtained and unsatisfied low protons conducting ability for them. To solve it, one strategy was the preparation of composite

membranes comprising of these LMP materials and Nafion polymer. It shows useful proton conductivity, but the proton conductivity of the composite membrane will be between that of Nafion and LMP membranes. Alternatively, the LMP membrane was applied on the surface of Nafion membrane, but resulted in a big decrease of proton conductivity compared to Nafion membrane. On the other hand, the performances of DMFC with LMP membrane are typically much lower than that of DMFC with Nafion membrane, in spite of the superiority of low methanol permeation of LMP membrane. It is mainly due to the low proton conductivity in the vicinity of the interfaces between LMP and Nafion polymers [5,6]. Therefore, the proton transfer process between Nafion and LMP should be studied further.

In this study, Nafion/sPPL composite membrane is used to investigate the proton transfer in the interface of Nafion and sPPL. The experimental results confirm that the proton transfer is very difficult in the interface between microphases of Nafion and sPPL.

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The addition of Nafion into sPPL not only enhances the proton conductivity of the composite membrane, but also changes the microstructure of the sPPL in the composite membrane.

2. Materials and methods

2.1. Materials

The sulfonated polypyrrolone (sPPL) was provided by S. Zhang's group, and 5 wt.% (w/v) of Nafion® solution was purchased from Du Pont Co. All other chemicals were of analytical grade and used without further purification. Dimethyl formamide (DMF) was purchased from Beihua Fine Chemical, Beijing, China. The composite membranes were obtained by casting on a glass substrate.

2.2. Preparation of the Nafion–sPPL composite membrane

5 wt.% Nafion DMF solution was obtained via solvent evaporation of the Nafion solution. In details, 5 wt.% Nafion® solution (2 ml) and DMF (2 ml) were sequentially added to a beaker (10 ml volume), which was followed by stirring for 1 h at room temperature and ambient conditions. The mixture was evaporated at 80 °C for several hours until the volume of the mixture reduced to 2 ml. Subsequently, 5 wt. % sPPL in DMF solution (2 ml) was added into the beaker and then the mixture was stirred for another 3 h. The mixture was evaporated at 80 °C for 2 days and then the Nafion–sPPL composite membrane (NP membrane) was obtained. The composite NP membranes with different Nafion/sPPL ratios were named as NP11 membrane (Nafion: sPPL = 1:1, w/w) and NP12 membrane (Nafion:sPPL = 1:2, w/w), respectively. For the NP11 membrane, it was also treated by annealing at 140 °C (>the glass transition temperature(T_g) of Nafion polymer, that is 130 °C) for 3 h in an oven (named as A-NP11 membrane), and then it was immersed into the deionized water at room temperature.

2.3. Atomic force microscopy (AFM)

To examine the surface morphology of the membranes, a SPI3800N atomic force microscope (AFM) instrument (Seiko Instrument Inc.) was employed in the tapping mode with a 2 N m⁻¹ probe and at a scan rate of 1.44 Hz under ambient conditions.

2.4. X-ray diffraction (XRD) measurements

XRD measurements were performed using a conventional diffractometer (Rigaku D/maximum 2500 VPC) that employs Ni-filtered Cu K α radiation. The dried membrane samples were mounted onto an aluminum sample holder. The scanning angle ranged from 5° to 30° with a scanning rate 2° min⁻¹. All spectra were taken at ambient temperature (22 ± 2 °C).

2.5. Conductivity measurements

The proton conductivity of the membranes was measured with a four-electrode conductivity cell that had two outer gold wires for current and two inner gold wires for voltage. The AC impedance spectra were measured using a Princeton Applied Research Model 273A Potentiostat (Model 5210 frequency response detector, EG&G PARC, Princeton, NJ) in the frequency range of 100 Hz to 100 kHz, with an AC perturbation voltage of 10 mV. The proton conductivity (σ) of the membrane was calculated using Equation (1):

$$\sigma = L/RA \quad (1)$$

where L , R , and A are the distance between the two inner gold wires, the in-plane resistance of the membrane, and the cross-sectional area of the membrane, respectively [7].

2.6. Water uptake test

The first step was to completely dry the membranes at 80 °C for 3 h before weighing them. After that, the membrane sample was placed into deionized water at ambient temperature for 3 h to allow water uptake. The swollen membrane was then taken out of the water and quickly wiped using filter paper to remove the remaining water on both sides of the membrane; the swollen membrane was then weighed. The quantity of water uptake inside the membrane was calculated according to Equation (2):

$$\text{Water Uptake(\%)} = 100 \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \quad (2)$$

where W_{wet} and W_{dry} are the weights of the membrane after and before water uptake, respectively.

3. Results and discussion

The proton conductivity is one of the most crucial parameters for characterizing a proton exchange membrane. In our studies, the proton conductivities of the NP membranes were measured and shown in Fig. 1. As depicted, by adding Nafion ionomer, the proton conductivity of the NP 11 membrane was enhanced by 34% compared to that of the sPPL membrane. Such proton conductivity enhancement benefits from the formation of proton conductive channels by addition of the Nafion ionomer. The enhanced proton conductivity of the composite membrane indicates that the binary NP membrane has the uniform microstructure and the proton conductive property of Nafion ionomer is not destroyed by the nearby sPPL. Assuming that there is no interaction between Nafion and sPPL, the proton conductivity of NP11 membrane can be calculated by Equation (3) as follows:

$$\sigma_{\text{NP11 membrane}} = \frac{\sigma_{\text{Nafion}}}{2} + \frac{\sigma_{\text{sPPL}}}{2} \quad (3)$$

While the proton conductivity of Nafion membrane σ_{Nafion} is 0.07 S cm⁻¹ and the proton conductivity of sPPL membrane σ_{sPPL} is 0.025 S cm⁻¹, the proton conductivity of composite membrane

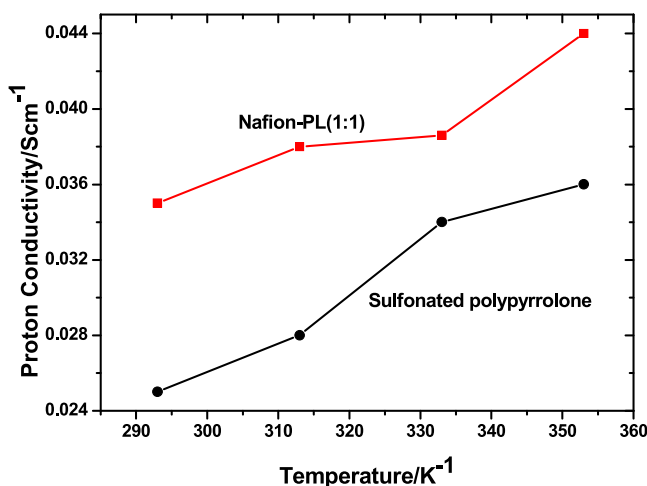


Fig. 1. The proton conductivity of the NP11 membrane and the sulfonated polypyrrolone membrane at different temperatures.

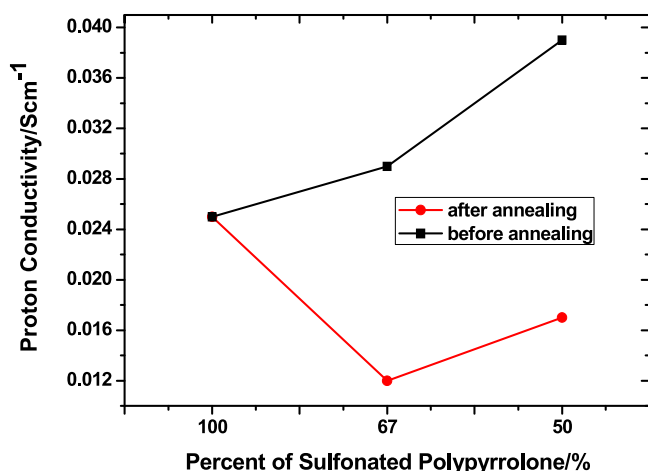


Fig. 2. The proton conductivity of the NP membranes with different sulfonated polypyrrolone percent (before and after annealing treatment).

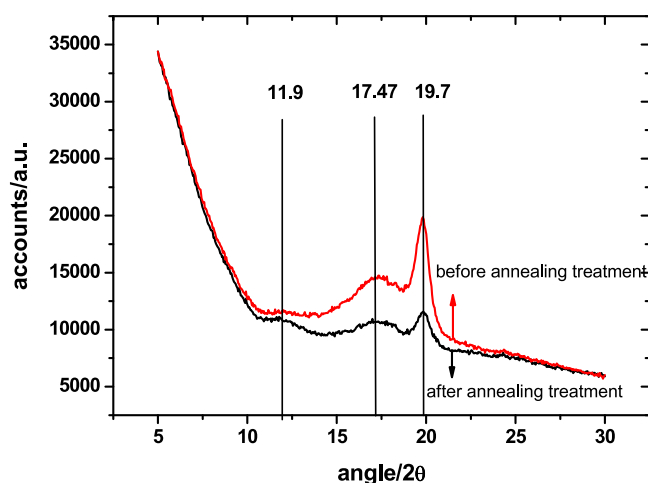


Fig. 3. The XRD measurements of the NP11 membrane and the A-NP11 membrane.

σ_{NP11} membrane in principle should be 0.047 S cm^{-1} by calculation. The experimental result of σ_{NP11} membrane, however, is only 0.035 S cm^{-1} . This result indicates that the sPPL indeed is covered by Nafion polymer in the microstructure of the NP11 membrane.

Fig. 2 shows the effect of the annealing treatment on the proton conductivities of the NP11 and NP12 membranes. As shown, after the annealing treatment, the proton conductivity of the NP11 and NP12 membranes is decreased by 58% and 56%, respectively. It is obvious in that the annealing treatment renders the proton conductivity of the NP12 membrane even lower than that of pure sPPL membrane. This phenomenon indicates that the annealing treatment could destroy the uniform structure of the composite membrane, leading to the formation of phase separation microstructure of the NP membranes.

In order to investigate the microstructure changes of the NP membranes by annealing treatment, wide-angle XRD was measured to provide some information about the morphological evolutions of the membrane. Fig. 3 shows the XRD patterns of the membranes before and after annealing treatment. As shown, three broad XRD peaks located at ca. 11.9° , 17.5° , and 19.7° are detected for the NP11 membrane before and after the annealing treatment, which corresponding to the different interchain spacing of the polymer species, according to Equation (4) shows below [8]:

$$2d \sin \theta = n\lambda, \quad n = 1, 2, 3, \dots \quad (4)$$

The same XRD peak positions imply that there is no change in the crystal structure of the polymer species of the membranes before and after annealing treatment. However, the relative intensity enhancement of the lower angles after annealing treatment of the NP membranes indicates the overall increase of low spacing region for the polymer chains of the composite membrane. In view of the polymer chain structure difference between Nafion and sPPL, such variations can be attributed to the microphase separation formed by the annealing treatment, which is further confirmed by the AFM tests. Fig. 4 shows the AFM images of the NP11 membrane before and after annealing treatment. The non-treated NP11 membrane displays a uniform morphological structure shown Fig. 4a. After annealing treatment (corresponding to the A-NP11 membrane), the morphology changes to a spherules structure, which implies the aggregation of polymer chains within the A-NP11 membrane. The aggregation of polymers interrupts the proton conductive channel within the composite membrane, resulting in the lowering of the proton conductivity.

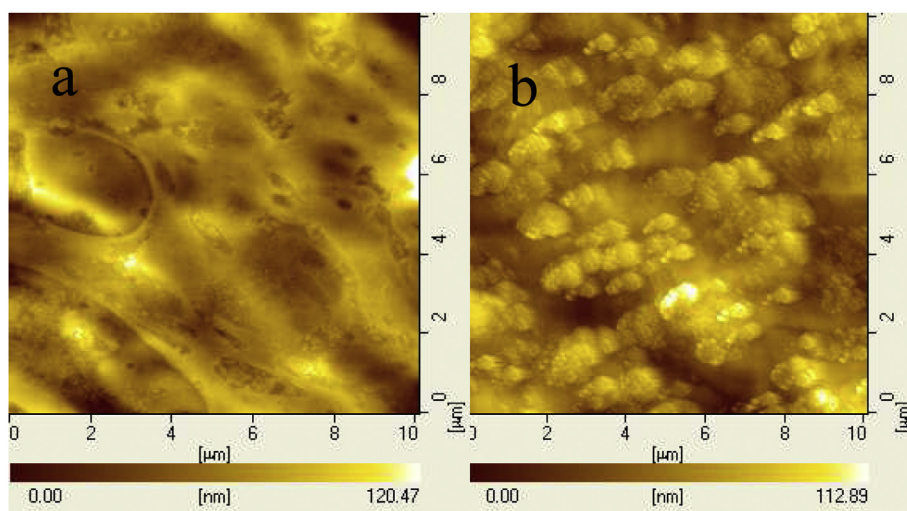
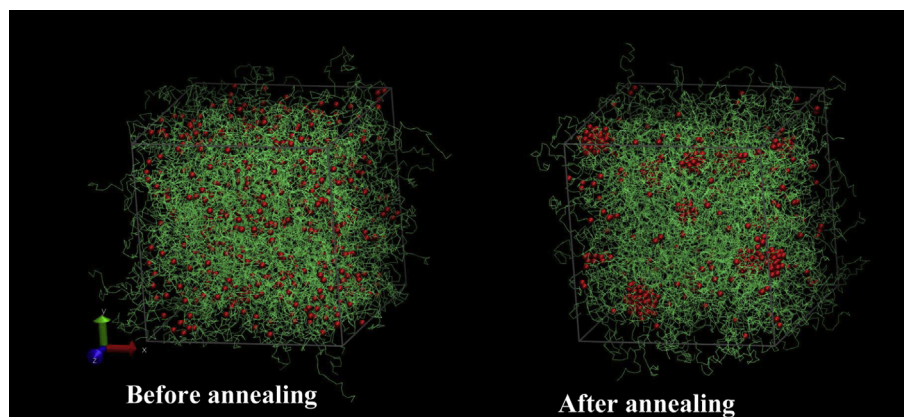


Fig. 4. The AFM images of the NP11 membrane (a) and the A-NP11 membrane (b).



Scheme 1. The 3D structure evolutions of the NP11 membrane (before and after annealing treatment).

Except for the phase separation mentioned above, other issue especially the water uptake evolution may also play roles for the lowered proton conductivity and should be considered. However, our results confirmed that there is just very slightly variation for this parameter before and after annealing treatment for the NP11 and NP12 composite membranes. As measured, for NP11 and NP12 membranes, the water uptake levels are 25.8%, 26.7% (before annealing) and 24.9%, 26.3% (after annealing), respectively. Accordingly, it is suggested that such small change in water uptake should not be the main origins accounting for the distinctly lowered proton conductivity detected.

The formation process may be simply expressed as follows. Before the annealing treatment, the Nafion ionomer is evenly distributed in the structures of sPPL. The proton conductive property is not destroyed by the sPPL. However, after the annealing treatment, the formation of microphase separation leads to a distinct Nafion aggregation. Therefore, some of the proton conductive channels are destroyed, which deteriorates the overall proton conductivity of the NP membranes. Scheme 1 depicts the 3D microstructure evolutions before and after the annealing treatment. Compared with the huge polymer chains of sPPL (green color), Nafion is expressed as particles (red color). Before annealing treatment, Nafion disperses in the network of sPPL. As the annealing treatment occurs, Nafion turns into the viscoelastic state and then agglomerates in together. After the annealing treatment, the interface between Nafion agglomerate and sPPL is formed, which is adverse to the proton transfer.

4. Conclusion

The annealing treatment is proved to induce phase separation of Nafion and sulfonated polypyrrolone in the Nafion/sulfonated polypyrrolone composite membrane, leading to the occurrence of interface proton transfer resistance between these two polymers.

The micro-scale phase separation plays a negative effect on the proton conductivity of the composite membrane, resulting in the decrease of proton conductivity by 58%. It is very difficult to transfer proton in the interface between Nafion and sulfonated polypyrrolone aggregates due to the different properties of the two distinct polymers. Therefore, the composite membrane should be applied less than the glass transition temperature of each polymer species. In DMFC, the polymer in catalyst layer should be consistent with the membrane. This conclusion is very helpful to the real application of the composite membrane as a proton exchange membrane in fuel cell.

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